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Adolphsen, Jens Quitzau; Gil, Vanesa; Sudireddy, Bhaskar Reddy; Chatzichristodoulou, Christodoulos

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DTU Energy
Department of Energy Conversion and Storage

Development of novel High Temperature and Pressure Alkaline Electrolysis Cells (HTP-AEC)

Jens Q Adolphsen (jenqui@dtu.dk); Vanesa Gil, Bhaskar R. Sudireddy and Christodoulos Chatzichristodoulou (ccha@dtu.dk)

Introduction

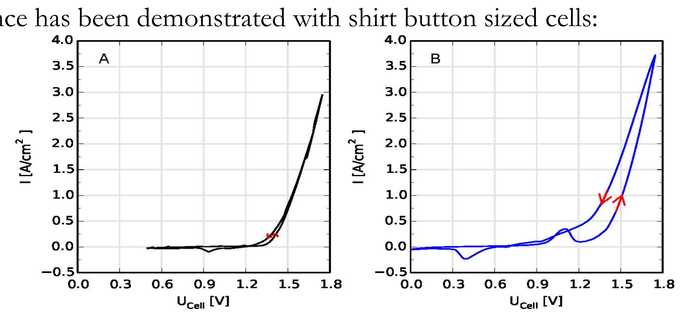
Background

- A HTP-AEC with gas diffusion electrodes (metal foams) and an aqueous KOH electrolyte immobilized in a mesoporous ceramic matrix structure has been developed at DTU Energy.
- Very high current density and performance has been demonstrated with shirt button sized cells:

Record data from earlier work [1]:

3.75 A/cm² at 1.75 V with

η_{el} *= 85 % (200°C, 20 bar) [1]*



Motivation

- High temperatures (200°C) increase the activity of the electrodes and the conductivity of the electrolyte significantly.
- A cell that allows for high efficiency and current density simultaneously using non-noble metals.

Challenges

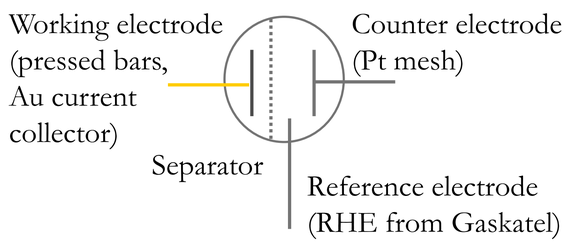
- Corrosion issues at the oxygen electrode. Identification of more stable materials, which also show sufficiently high catalytic activity towards the oxygen evolution reaction.
- Processing of cell layers with optimized microstructure using a low cost & scalable processing method.

The experiments

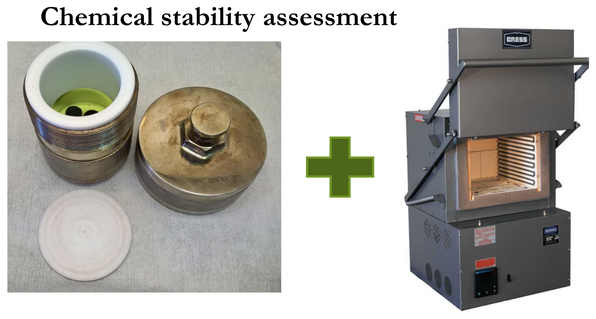
Electrode materials for the oxygen electrode

- Electrode materials (electrocatalysts) based on La, Ni and Fe for the oxygen evolution reaction (OER) have been identified and evaluated.
- The electrochemical activity of the materials has been tested at room temperature and pressure conditions in N_2 atmosphere using densely sintered pellets polished down to 1 µm roughness.
- The chemical stability of the powder , immersed in 45 wt% KOH, and heated in an autoclave to 220°C has been examined comparing XRD patterns before and after.

Three-electrode setup for electrochemical characterization

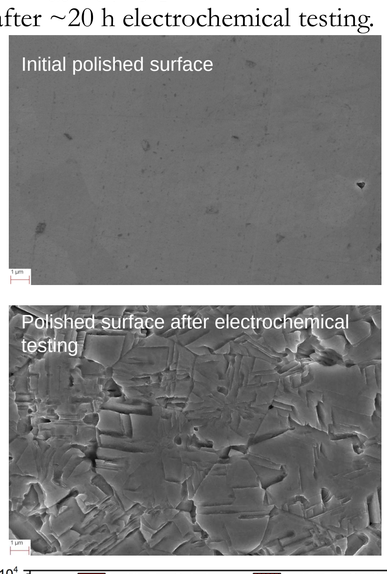


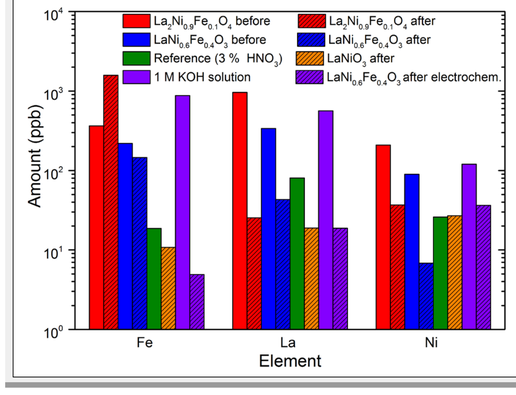
Chemical stability assessment

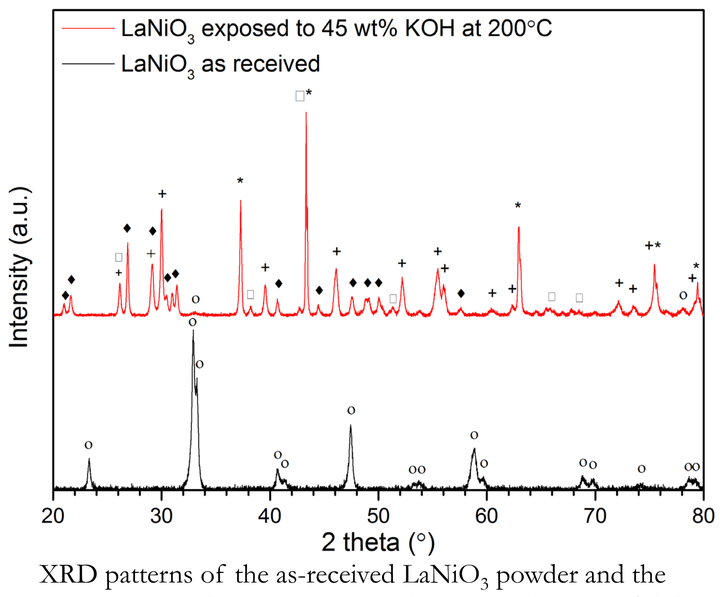


Results – chemical stability

$LaNi_{0.6}Fe_{0.4}O_3$ pellet surface before and after ~20 h electrochemical testing.



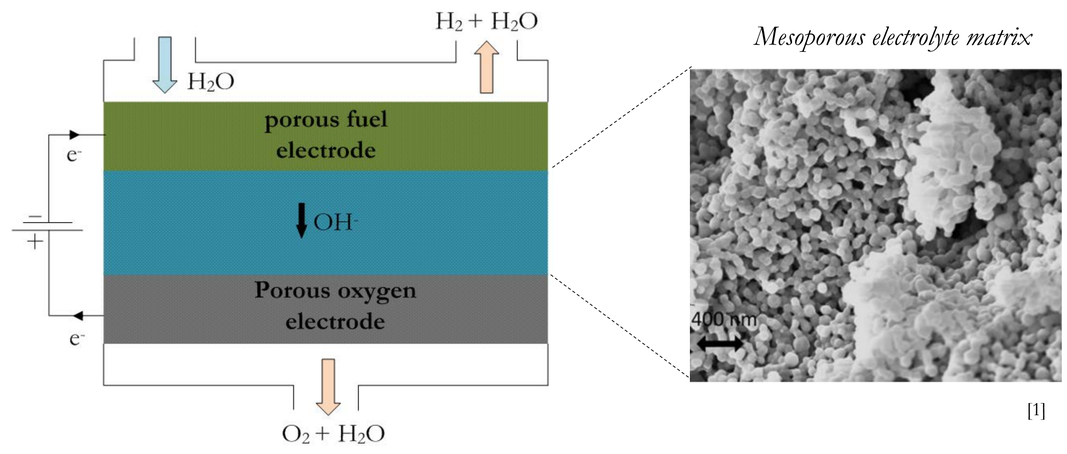




XRD patterns of the as-received $LaNiO_3$ powder and the same powder after exposure to 45 wt% KOH at 220 °C for 1 week. The symbols represent the following phases: ○$LaNiO_3$, ♦ LaO(OH), □ NiO(OH), + La_2O_3, * NiO. The $LaNi_{0.6}Fe_{0.4}O_3$ and $La_2Ni_{0.9}Fe_{0.1}O_4$ powder showed similar decomposition behaviour though at a slower rate.

ICP analysis of supernatants from the KOH solution used for the chemical stability testing. If any dissolution is happening the ions seem to be consumed by the decomposed products.

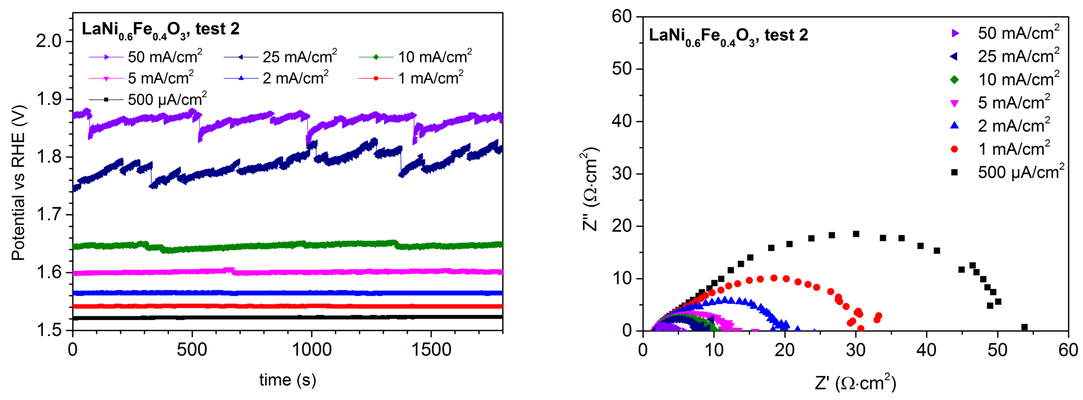
The cell concept



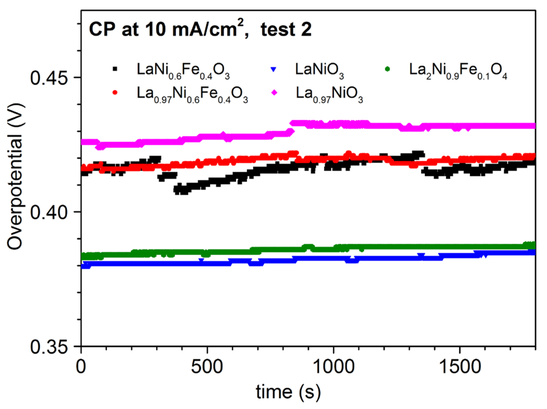
[1]

The mesoporous electrolyte matrix contains the KOH electrolyte. The porous electrodes will allow some infiltration of the electrolyte into the electrode to increase the surface area where the electrochemical reactions take place.

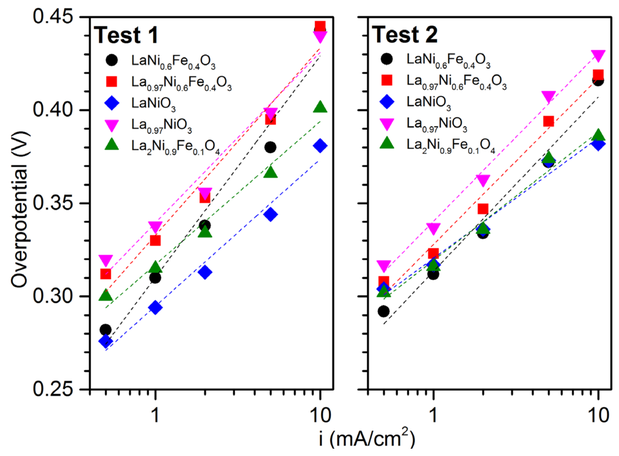
Results - Electrochemical activity towards the OER



The iR-corrected chronopotentiostatic measurements of $LaNi_{0.6}Fe_{0.4}O_3$ and the Nyquist plot of the EIS measurements performed after each chronopotentiostatic measurement. Current densities are based on geometric surface areas.



Comparisson of the 2nd set of chronopotentiostatic tests performed at 10 mA/cm². $LaNiO_3$ could not be sintered dense without decomposition so it is a multiphase of mainly $LaNiO_3$, NiO and La_2NiO_4



The tafel plot of the measurements. The fit is from 0.5 – 10 mA/cm². There is a slight increase in the tafel slope above 2 mA/cm² which is then not accounted for.

The calculated Tafel fit parameters (E = a +b log[i]) from the tafel plot together with the overpotential, η, at 10 mA/cm². The state-of-the-art, IrO_x, and two of the best performing non-noble oxygen evolution catalysts are also included as benchmarking.

Material	b (V/dec)	a	R²	η (V) @ 10 mA/cm²
$LaNiO_3$	0.083	0.30	0.97	0.38
$La_{0.97}NiO_3$	0.092	0.34	0.97	0.44
$LaNi_{0.6}Fe_{0.4}O_3$	0.13	0.31	0.95	0.44
$LaNi_{0.6}Fe_{0.4}O_3$	0.11	0.33	0.97	0.45
$La_2Ni_{0.9}Fe_{0.1}O_4$	0.079	0.32	0.98	0.40
IrO_x [2]	-	-	-	0.32
$Ni_{0.9}Fe_{0.1}O_x$ [3]	0.030	-	-	0.34
$PrBaCo_2O_{5+x}$ [4]	~0.07	-	-	~0.38

Outlook

Processing of porous oxygen electrodes

Based on the electrochemical screening $LaNi_{0.6}Fe_{0.4}O_3$ is going to be used as oxygen evolution electrocatalyst. The microstructure of the oxygen electrode is going to be optimized using the processing method screen printing. An electrode with a bimodal porosity distribution is envisioned to allow for electrolyte infiltration (~10-100 µm pore sizes) and gas diffusion (2-10 µm pore sizes) of evolved oxygen.

Successful fabrication and electrochemical characterization of up-scaled cells (5 x 5 cm²) with the microstructurally optimized oxygen electrode is the expected outcome of the project.

DTU Energy, Technical University of Denmark
Department of Energy Conversion and Storage
Risø Campus
Frederiksborgvej 399, 4000 Roskilde

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